PRESSURE BROADENING AND SHIFTING COEFFICIENTS AS TESTS OF H2(D2)-He POTENTIAL ENERGY SURFACES

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PRESSURE BROADENING AND SHIFTING COEFFICIENTS AS TESTS OF H_2-He POTENTIAL ENERGY SURFACES

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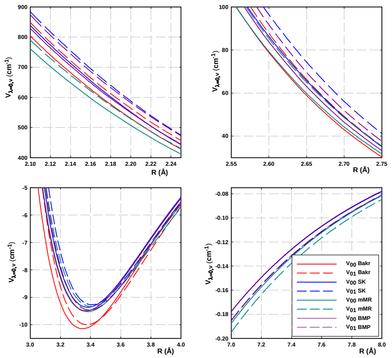
We have used the Schaefer and Köhler[1] (SK),the modified Muchnick and Russek[2] (MR), the Boothroyd, Martin and Peterson[3] (BMP), and the Bakr, Smith and Patkowski[4] H_2-He potential energy surfaces in order to calculate, using the close coupling method, pressure broadening and shifting coefficients. The helium pressure broadening and shifting generalized cross sections of the isotropic raman Q(1) lines of the fundamental of D_2 and H_2 as well as the purely rotational Stokes $S_0(1)$ line of H_2 were computed. We have decomposed the pressure broadening cross-sections in a purely inelastic and a purely dephasing, including a vibrational one for the Q lines, contributions. Such a decomposition allows us to better understand the main differences that exist between these potentials. The old Schaefer and Köhler PES and the most recent one, namely the Bakr et al PES, give close results in quite good agreement with available experimental data.

1. PESs used

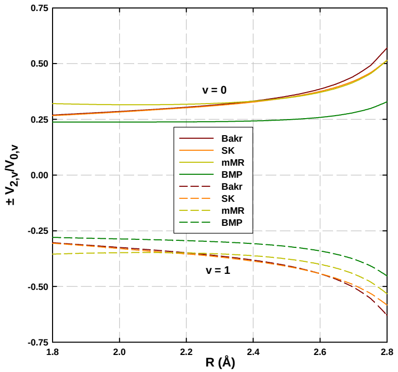
Comparison of the isotropic components in v=0 and in v=1 (j=j'=0, no centrifugal distortion):



$$V(r,R,\theta)=\sum_{\lambda\,even} V_\lambda(r,R)P_\lambda(\cos\theta)$$

$$V_{\lambda,vj,vj'}(R)=\int dr\,\chi_{vj}(r)V_\lambda(r,R)\chi_{vj'}(r)$$

Comparison of the ratio of the first anisotropic Component to the isotropic one in v=0 and v=1:



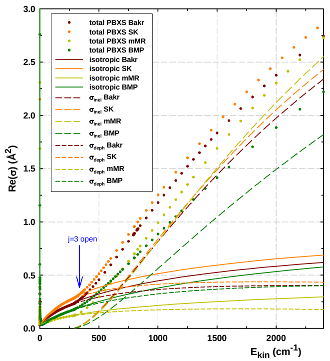
The modified MR PES shows the less differences in its isotropic parts in v=0 and v=1 while the SK PES shows the most differences.
The modMR PES differs significantly from the others at long range.
The BMP PES is the less anisotropic PES.

2. Pressure broadening and shifting cross-sections and coefficients

$$\sigma^{(n)}(v_ij_iv_fj_f;E_{kin})=\sigma_{inelastic}(v_ij_i,v_fj_f;E_{kin})+\sigma^{(n)}_{dephasing}(v_ij_i,v_fj_f;E_{kin})\qquad \sigma^{(n)}_{PB}(if;E_{kin})=\mathrm{Re}\left(\sigma^{(n)}(if;E_{kin})\right)\qquad \sigma^{(n)}_{PS}(if;E_{kin})=\mathrm{Im}\left(\sigma^{(n)}_{dephasing}(if;E_{kin})\right)$$

$$\sigma_{inelastic}(v_ij_i,v_fj_f;E_{kin})=\frac{1}{2}\left(\sum_{j_i'\neq j_i}\sigma(v_ij_i\to v_ij_i';E_{kin})+\sum_{j_f'\neq j_f}\sigma(v_fj_f\to v_fj_f';E_{kin})\right)\qquad \gamma+i\delta=n_b\bar{v}\left(\frac{1}{k_BT}\right)^2\int dE_{kin}E_{kin}\exp(-E_{kin}/k_BT)\sigma^{(n)}(if;E_{kin})$$

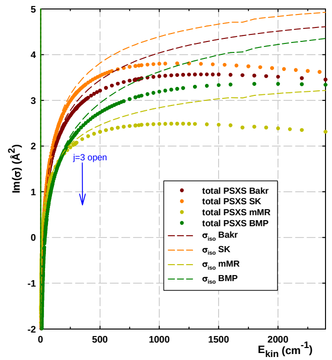
3. Raman isotropic Q(1) line of the fundamental band of D_2



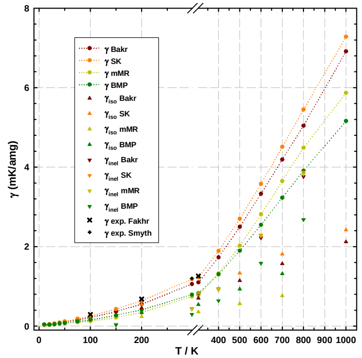
Contributions to the cross-sections

widths:
total
inelastic
elastic dephasing
vibrational dephasing (ΔV_{iso})

shifts:
total
vibrational dephasing (ΔV_{iso})

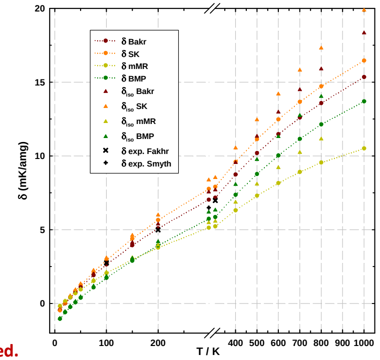


Pressure broadening coefficients of the Q(1) of D_2 in He



At low T most of the broadening and shifting arise from the isotropic parts but as T increases the effects of the anisotropy and related inelastic collisions increase.

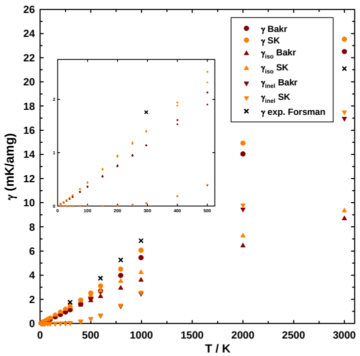
Pressure shifting coefficients of the Q(1) of D_2 in He



The modMR and BMP PESs are rejected.

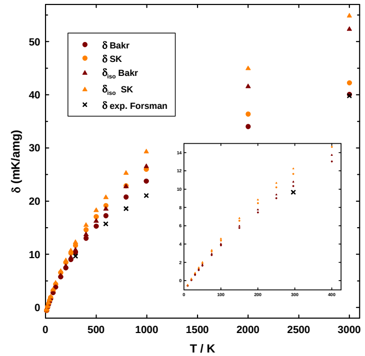
4. Raman isotropic Q(1) line of the fundamental band of H_2 in He

Pressure broadening coefficients of the Q(1) of H_2 in He



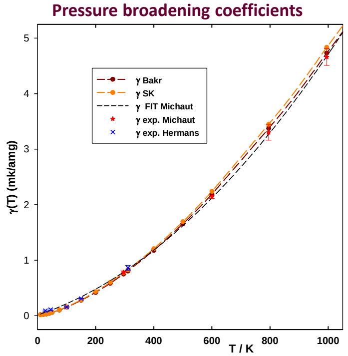
The SK PES gives better agreement with the experimental[7] PB coefficients while the Bakr PES provides better agreement for the PS coefficients.

Pressure shifting coefficients of the Q(1) of H_2 in He



5. Stokes $S_0(1)$ line of H_2 in He

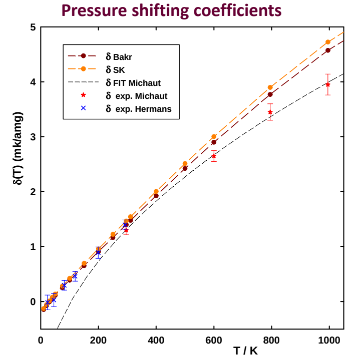
Pressure broadening coefficients



In this case it is important to take into account the centrifugal distortion especially for the shifts.

The SK and Bakr et al PESs lead to very close results in good agreement with the experimental values[8,9] over the full range of T.

Pressure shifting coefficients



Work in progress proves that the relative differences between PB coefficients derived with the SK and Bakr PESs are smaller than relative differences between coefficients taking into account inhomogeneous broadening or not. Including the inhomogeneous mechanism leads to much better agreement with observed widths.

[1] J. Schaefer and W.E. Köhler, Physica A 129, 469 (1985)
[2] P. Muchnick and A. Russek, J. Chem. Phys. 100, 4336 (1994)
[3] A.I. Boothroyd, P.G. Martin, M.R. Peterson, J. Chem. Phys. 119, 3187 (2003)
[4] B.W. Bakr, D.G.A. Smith, K. Patkowski, J. Chem. Phys. 139, 144305 (2013)
[5] S.H. Fakhr-Eslam, G.D. Sheldon, P.M. Sinclair, J.R. Drummond, A.D. May, J.Q.S.R.T. 68, 377 (2001)
[6] K.C. Smyth, G.J. Rosasco, W.S. Hurst, J. Chem. Phys. 87, 1001 (1987)
[7] J.W. Forsman, J. Bonamy, D. Robert, J.-Ph. Berger, R. Saint-Loup, H. Berger, Phys. Rev. A. 52, 2652 (1995)
[8] P.W. Hermans, A. Van Die, H.F.P. Knaap, J.J.M. Beenakker, Physica A 122, 233 (1985)
[9] X. Michaut, R. Saint-Loup, H. Berger, M.-L. Dubernet, J. Bonamy, D. Robert, J. Chem. Phys. 109, 951 (1998)